

4) PCT/EP 2005/001672

Corresp. US 4,583,984

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification³ : D01F 11/02, 2/00; C08B 15/06	A1	(11) International Publication Number: WO 83/ 03433 (43) International Publication Date: 13 October 1983 (13.10.83)
(21) International Application Number: PCT/FI83/00028 (22) International Filing Date: 25 March 1983 (25.03.83) (31) Priority Application Number: 821106 (32) Priority Date: 30 March 1982 (30.03.82) (33) Priority Country: FI (71) Applicant (for all designated States except US): NESTE OY [FI/FI]; Keilaniemi, SF-02150 Espoo 15 (FI). (72) Inventors; and (75) Inventors/Applicants (for US only) : TURUNEN, Olli, T. [FI/FI]; Pehtorintie 2, SF-06400 Porvoo 64 (FI). HUTTUNEN, Jouko, I. [FI/FI]; Kompassitie 12, SF-06150 Porvoo 15 (FI). EKMAN, Kurt [FI/FI]; Jokikatu 23 B 10, SF-06100 Porvoo 10 (FI). EKLUND, Vidar [FI/FI]; Raatimiehenkatu 10 A 6, SF-06100 Porvoo 10 (FI). MANDELL, Leo [FI/FI]; Piispankatu 8-10 D 31, SF-06100 Porvoo 10 (FI).		(74) Agent: FORSSÉN & SALOMAA OY; Uudenmaankatu 40 A, SF-00120 Helsinki 12 (FI). (81) Designated States: AT (European patent), BR, DE (European patent), FR (European patent), GB (European patent), JP, NO, SE (European patent), SU, US. Published <i>With international search report.</i>
(54) Title: PROCEDURE FOR TREATING CELLULOSE DERIVATIVE FIBRES (57) Abstract The present invention concerns improving the properties of cellulose carbamate fibres. The wet strength properties in particular can be improved by treating the fibres with alkalis or organic bases, aiming to reduce the number of carbamate groups. The procedure may also be applied in the manufacturing of regenerated cellulose fibres.		

FOR THE PURPOSES OF INFORMATION ONLY

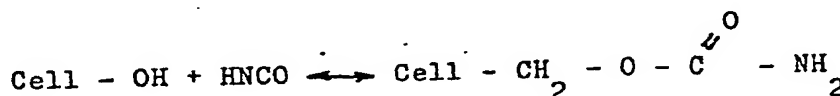
Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	LI	Liechtenstein
AU	Australia	LK	Sri Lanka
BE	Belgium	LU	Luxembourg
BR	Brazil	MC	Monaco
CF	Central African Republic	MG	Madagascar
CG	Congo	MR	Mauritania
CH	Switzerland	MW	Malawi
CM	Cameroon	NL	Netherlands
DE	Germany, Federal Republic of	NO	Norway
DK	Denmark	RO	Romania
FI	Finland	SE	Sweden
FR	France	SN	Senegal
GA	Gabon	SU	Soviet Union
GB	United Kingdom	TD	Chad
HU	Hungary	TG	Togo
JP	Japan	US	United States of America
KP	Democratic People's Republic of Korea		

Procedure for treating cellulose derivative fibres

The present invention concerns a procedure for treating cellulose derivative fibres. More specifically, the invention concerns a procedure for regulating the properties of cellulose carbamate fibres. Furthermore, the invention concerns a novel procedure for manufacturing regenerated cellulose fibres.

In the Finnish patent application Nos. 793226 and 810226 is disclosed a procedure for manufacturing an alkali-soluble cellulose derivative from cellulose and urea at elevated temperature. The procedure is based on the fact that on heating urea to its melting point or to a higher temperature it begins to decompose into isocyanic acid and ammonia. Isocyanic acid in itself is not a particularly stable compound: it tends to trimerize into isocyanuric acid. Furthermore, isocyanic acid also tends to react with urea, whereby biuret is formed. Isocyanic acid also reacts with cellulose, producing an alkali-soluble cellulose derivative which is called cellulose carbamate. The reaction may be written as follows:-



The cellulose compound thus produced, cellulose carbamate, may be dried subsequent to washing and stored even over prolonged periods, or it may be dissolved in an aqueous alkali solution for manufacturing fibres, for instance. From this solution can be manufactured cellulose carbamate fibres or films by spinning or by extruding, in like manner as in the viscose manufacturing process. The keeping quality of cellulose carbamate and its transportability in dry state afford a great advantage compared with cellulose xanthate in the viscose process, which cannot be stored nor transported, not even in solution form.



If, for instance, continuous fibre or filament manufactured from cellulose carbamate appropriate for textile uses is desired, the carbamate is first dissolved in alkali, e.g. in aqueous sodium hydroxide solution. From this solution may then be precipitated
5 fibre or film, for instance in like manner as in the manufacturing of viscose fibre cellulose is regenerated from the NaOH solution of cellulose xanthate. In this connection, the cellulose carbamate solution is spun through spinnerets into an acid precipitation bath, which causes precipitation of the cellulose carbamate. The
10 precipitation may also be accomplished into lower alcohols such as methanol, ethanol or butanol, or into hot aqueous salt solutions.

The properties of precipitated fibres are substantially influenced by the nitrogen content of the fibre, that is, the number of carbamate groups in the cellulose chain. It has been found that the
15 carbamate groups increase the sensitivity of the fibres to water and, simultaneously, they impair the wet properties of the fibres. In some cases, this is even an advantage, whereas in other cases it is detrimental because, for instance in textile uses, the fibres
20 are most often expected to have good wet strength.

The object of the present invention is a procedure by which the properties of cellulose carbamate fibres, in particular their wet properties, can be regulated as desired so that fibres suitable for
25 each purpose are obtained. The procedure according to the invention for regulating the properties of cellulose carbamate fibres is characterized in that the fibres are treated with alkali or with an organic base.

30 By the aid of an alkali treatment according to the invention, the carbamate groups of the cellulose carbamate can be removed to the desired degree. Thus for instance the wet strength of the fibres substantially increases, while the wet stretchability decreases.

If, again, for instance fibres for non-woven purposes are desired
35 which have good water absorption capacity and swelling capacity, the alkali treatment of the invention may be carried out in a milder form.



It is possible to carry the alkali treatment of cellulose carbamate fibres so far that a near complete removal of the carbamate groups from the fibres takes place. A fibre has then been obtained of which the solubility in alkali has gone down to the same level as that of regenerated cellulose fibres obtained by the viscose method, that is, less than 10%. In fact, a regenerated cellulose fibre is concerned, manufactured in a different way from the regenerated cellulose fibre of the viscose method. Thus, an object of the invention is a new process for manufacturing regenerated cellulose fibres comprising the treatment of cellulose carbamate fibres with an alkali or an organic base for substantially removing the carbamate group from the fibres. In a broader sense, by the invention is provided a new process for manufacturing regenerated cellulose fibres, this process being characterized by the following steps:

15 dissolving cellulose carbamate in alkali, spinning or precipitating the carbamate solution to cellulose carbamate fibres or filaments, and conversion of the cellulose carbamate fibres or filaments to regenerated cellulose by treating the fibres with alkali or with an organic base. In the different steps of the process any procedures or means may be used which result in accomplishment of said method steps, and as examples may be mentioned the procedures disclosed in the Finnish Patents No. 61033 and 62318 and Finnish patent applications No. 814208 and 814209.

25 Towards regulating the properties of cellulose carbamate fibres as taught by the invention, any alkali or organic base may be used. Sodium hydroxide and potassium hydroxide are suitable alkalis, and among organic bases may be mentioned as examples tetramethylammonium hydroxide and ethylene diamine. The amount of alkali or base required depends on the alkali used in each case. When using sodium hydroxide, the concentration of the alkali solution is preferably less than 2%, because larger NaOH quantities may adversely affect the properties of the fibre. The suitable NaOH quantity is in the range 0.1 to 2%. Potassium hydroxide does not act as powerfully as sodium hydroxide, and when it is used the suitable quantity is in the range of 0.1 to 4%. Organic bases are not as powerful as the above-mentioned, and therefore, the concentration range appropriate



in their case may vary in the range of 0.1 to 10%.

The treatment time and temperature depend greatly on how large a proportion of the carbamate groups one desires to eliminate. For instance, a treatment at room temperature may be applied, although in that case the required treatment times may become quite long. The treatment times can be shortened by raising the temperature, even down to a few minutes. A temperature suitable in practice is mostly from room temperature to 100°C, but higher temperatures may be used if treatment means capable of containing pressure are at disposal.

The invention is described more in detail in the embodiment examples included. The percentages stated in the examples are to be understood as per cent by weight. The wet strengths of staple fibres mentioned in the examples were determined by procedures which are readable in: BISFA (International Bureau for the Standardization of Man-Made Fibers), Internationally agreed method for testing regenerated cellulose and acetate staple fibres, 1970 Edition. The fibres were air-conditioned at 23°C and 50% relative humidity.

Example 1

Cellulose carbamate fibres were manufactured as follows. Bleached spruce sulphate cellulose (400 g) with DP brought to the level of 390 by the aid of γ radiation was impregnated at -40°C with 3.3 litres of liquid ammonia in which had been dissolved 400 g urea. The cellulose was kept in this solution below the boiling point of ammonia for six hours, whereafter it was taken into room temperature. On evaporation of the ammonia, the urea cellulose was placed in a vacuum oven at 135°C for three hours. An air flow produced by a water jet pump passed through the oven all the time.

The reaction product was washed with methanol, three times with water and once with methanol. The air-dry product had DP 340 and nitrogen content 1.7%. A solution was prepared by dissolving the



cellulose carbamate thus manufactured in 10% NaOH solution, containing also ZnO for better solubility. The carbamate content of the solution was 5.5% and the ball viscosity, 50 seconds. Of the solution was determined the clogging number by the procedure presented in: H. Sihtola, Paperi ja Puu 44 (1962), No. 5, p. 295-300. The clogging number of the solution was found to be 495. The solution was pressed into sulphuric acid solution through a spinneret with 100 holes having diameter 0.09 mm. The precipitating solution contained 10% sulphuric acid, 7% aluminium sulphate and 20% sodium sulphate.

In connection with precipitation, the fibres were stretched 0-80% to improve their strength properties. Subsequent to washing and drying, cellulose carbamate fibres A-G were obtained which were used in the other examples. In Table I are presented the manufacturing conditions of the fibres.

TABLE I

FIBRE	DISSOLVING		PRECIPITATION
	NaOH (%)	ZnO (%)	Stretching (%)
A	10	1,0	0
B	10	1,0	50
C	10	1,0	75
D	10	1,0	80
E	10	1,5	0
F	10	1,5	50
G	10	1,5	75

Example 2

Fibres manufactured as in Example 1 were treated with NaOH solutions having various concentrations. The wet properties of the fibres were determined before and after the alkali treatment. The



alkali solubility of the fibres was determined using the standard method SCAN - C2:61 and 5.5% NaOH solution.

5 In Table II following below are presented the properties of the fibres and after the NaOH treatment. The table reveals that alkali treatment of cellulose carbamate fibres improves the fibres' wet strength properties if the alkali concentration is at a reasonable level. When the alkali concentration goes up to 21%, the strength properties of the fibres deteriorate. When the alkali treatment is carried out at elevated temperature, better strength properties are achieved with considerably shorter treatment times. Stretching the fibres at the spinning phase also has a beneficial effect on the strength properties.

15 Example 3

As in Example 2, NaOH treatments of cellulose carbamate fibres were carried out using elevated temperatures. Table III gives the properties of the fibres before and after the alkali treatment. The table reveals that remarkably short treatment times are achieved using the temperature 100°C.

Example 4

25 As in Example 2, alkali treatments of cellulose carbamate fibres were carried out. Potassium hydroxide was used for alkali. Table IV presents the properties of the fibres before and after the alkali treatment.

30 The results reveal that potassium hydroxide is not quite as efficient as sodium hydroxide. Higher alkali concentrations than in the case of NaOH may be used in the treatment.

Example 5

35

As in Example 2, alkali treatments of cellulose carbamate fibres were carried out. Tetramethylammonium hydroxide was used as alkali.



Table V presents the properties of the fibres before and after the alkali treatment.

Example 6

5

Fibres manufactured as in Example 1 were treated with NaOH so that a substantial part of the carbamate groups were removed and the alkali solubility of the fibres was lowered to the level of regenerated fibres obtained in the viscose process. In Table VI are presented the properties of the fibres before the alkali treatment and the properties of the regenerated fibres after the alkali treatment.



TABLE III

Fibre	FIBRE CHARACTERISTICS BEFORE ALKALI TREATMENT					FIBRE CHARACTERISTICS AFTER ALKALI TREATMENT							
	Alkali solubil. %	Nitrogen content %	Wet strength cN/dtex	Distens. when wet %	Modulus when wet cN/dtex	Alkali conc. %	Temper- ature °C	Time h	Alkali solubil. %	Nitrogen content %	Wet strength cN/dtex	Distens. when wet %	Modulus when wet cN/dtex
A	86,3	1,1	0,8	53	3	0,5	23	70	75,0	0,3	0,8	17	8
C	86,9	"	0,9	10	13	0,5	"	"	52,9	0,3	1,4	10	14
"	"	"	"	"	"	2,0	"	"	6,7	0,2	0,9	9	9
D	86,8	1,0	1,1	15	14	0,25	40	5	77,1	0,8	1,3	13	14
"	"	"	"	"	"	0,50	"	"	62,3	0,5	1,2	10	15
"	"	"	"	"	"	0,75	"	"	44,8	0,5	1,4	11	16

TABLE III

FIBRE CHARACTERISTICS AFTER
ALKALI TREATMENT

ALKALI TREATMENT

FIBRE CHARACTERISTICS BEFORE
ALKALI TREATMENT

Fibre	Alkali solub.			Nitrogen content			Wet strength			Distens. when wet			Modulus		
	z	z	z	z	z	z	z	z	z	z	z	z	z	z	z
E	88,0	1,1	0,7	73	2	0,5	60	24	21,2	0,2	0,8	43	3		
F	"	"	0,9	30	7	"	"	"	18,7	"	1,2	13	12		
G	"	"	1,0	10	11	"	"	"	17,0	0,3	1,5	10	16		
D	86,8	1,0	1,1	15	14	"	100	0,05	39,1	0,4	1,5	12	15		
"	"	"	"	"	"	"	"	0,2	8,5	0,1	1,5	9	19		

TABLE IV

Fibre	FIBRE CHARACTERISTICS BEFORE ALKALI TREATMENT				ALKALI TREATMENT				FIBRE CHARACTERISTICS AFTER ALKALI TREATMENT			
	Alkali solub., %	Nitrogen content %	Wet strength cN/dtex	Distens. when wet %	Modulus when wet cN/dtex	Alkali conc. %	Time h	Temp- ature °C	Alkali content %	Wet strength cN/dtex	Distens. when wet %	Modulus when wet cN/dtex
B	88,0	1,1	0,8	32	7	0,5	72	22	77,6	1,0	19	10
"	"	"	"	"	"	1,0	"	"	59,5	1,0	18	9
"	"	"	"	"	"	2,0	"	"	29,5	1,1	15	10
F	"	"	0,9	30	"	0,5	0,2	100	38,5	1,1	12	11
"	"	"	"	"	"	"	1,0	"	12,1	1,2	12	12
"	"	"	"	"	"	2,0	0,2	"	22,0	1,1	12	11
"	"	"	"	"	"	"	1,0	"	7,3	1,2	12	11

TABLE V

Fibre	FIBRE CHARACTERISTICS BEFORE ALKALI TREATMENT					FIBRE CHARACTERISTICS AFTER ALKALI TREATMENT							
	Alkali solubilit. %	Nitrogen content %	Wet strength cN/dtex	Distens. when wet %	Modulus when wet cN/dtex	Alkali conc. %	Time h	Temper- ature °C	Alkali content %	Wet strength cN/dtex	Distens. when wet %	Modulus when wet cN/dtex	
F	88,0	1,1	0,9	30	7	0,5	72	22	88,0	0,6	1,0	21	6
"	"	"	"	"	"	1,0	"	"	74,6	0,5	1,0	18	7
"	"	"	"	"	"	2,0	"	"	67,0	0,3	1,0	18	7
"	"	"	"	"	"	0,5	0,2	100	50,0	0,3	1,0	18	9
"	"	"	"	"	"	2,0	0,5	"	16,8	0	1,2	13	11
"	"	"	"	"	"	"	1,0	"	-11,7	0,1	1,0	11	11

TABLE VI

FIBRE CHARACTERISTICS BEFORE ALKALI TREATMENT														ALKALI TREATMENT														FIBRE CHARACTERISTICS AFTER ALKALI TREATMENT													
Fibre	Alkali solubil.		Nitrogen content	Wet strength	Distens.	Modulus	Alkali conc.	Temper- ature	Time	Alkali conc.	Nitrogen content	Wet strength	Distens.	Modulus	Fibre		Alkali solubil.		Nitrogen content	Wet strength	Distens.	Modulus																			
	z	%													z	%	z	%					z	%	z	%	z	%	z	%											
A	86,3		1,1	0,8	53	3	2,0	23	70	7,1	0,1	0,7	17	8																											
D	86,8		1,0	1,1	15	14	0,5	100	0,25	6,1	0	1,6	10	15																											
"	"		"	"	"	"	"	"	1,0	3,8	0	1,4	8	17																											

Claims

1. Procedure for regulating the wet properties of cellulose carbamate fibres, characterized in that the fibres are treated with alkali or with an organic base.
- 5 2. Procedure according to claim 1, characterized in that cellulose carbamate fibres are treated with aqueous NaOH or KOH solution.
3. Procedure according to claim 2, characterized in that the fibres are treated with 0.1-2% NaOH or KOH solution.
- 10 4. Procedure according to claim 1, characterized in that carbamate fibres are treated with 0.1-10% tetramethylammonium hydroxide or with ethylene diamine.
- 15 5. Procedure according to any one of claims 1 to 4, characterized in that the treatment is carried out at elevated temperature.
6. Procedure towards manufacturing regenerated cellulose fibres, characterized in that cellulose carbamate fibres are treated with
20 alkali or with an organic base for substantially totally removing the carbamate groups.
7. Procedure for manufacturing regenerated cellulose fibres, characterized in that the procedure comprises the following steps:-
25 (a) dissolving cellulose carbamate in alkaline conditions,
(b) spinning or precipitating the cellulose carbamate solution to cellulose carbamate fibres or filaments, and
(c) treating cellulose carbamate fibres or filaments with alkali or
with an organic base for removing the carbamate groups and ob-
30 taining regenerated cellulose fibres or filaments.



INTERNATIONAL SEARCH REPORT

International Application No PCT/FI83/00028

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC 3		
D 01 F 11/02, D 01 F 2/00, C 08 B 15/06		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
IPC 3 US C1	C 08 B 15/06, 16/00, D 01 F 2/00, 2/02, 2/24, 11/00, 11/02 536:30, 56, 57	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
SE, NO, DK, FI classes as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT 14		
Category *	Citation of Document, 15 with indication, where appropriate, of the relevant passages 17	Relevant to Claim No. 16
A	FI, B , 61 033 (NESTE OY) 29 January 1982	
A, P	EP, A2, A3, 57 105 (NESTE OY) 4 August 1982	
<p>* Special categories of cited documents: 15</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search: *	Date of Mailing of this International Search Report *	
1983-06-23	1983-07-06	
International Searching Authority *	Signature of Authorized Officer 18	
Swedish Patent Office	Jack Hedlund	